

## Module - V

# Quantum physics

### NEED FOR QUANTUM PHYSICS

Classical physics was successful in explaining most of the observed physical phenomena. It describes the motion of particles, rigid body, motion of fluids etc. under the influence of appropriate forces. Phenomena of electromagnetism, thermodynamics, geometrical and physical optics were also successfully explained by Classical Mechanics. But it failed to explain the stability of atom and also the spectrum of hydrogen atom. It also doesn't hold well in the region of atomic dimensions.

So, in order to explain the physical phenomena in the atomic dimensions, a basic mathematical theory was accepted. This is known as Quantum Mechanics and subject matter concerning all this phenomenon is known as Quantum Physics. The quantum physics starting from microscopic world also successfully explains the macroscopic world.

### IMPORTANT OUTCOME OF QUANTUM PHYSICS:

- i. The Quantum Physics was first introduced by Max Planck in the year 1900 in an attempt to explain the observed energy distribution in the spectrum of black body radiation. The energy associated is given by,

$$E_n = nh\nu \quad \text{Where } n = 1, 2, 3, \dots$$

Where  $h$  = Planck's constant and  $\nu$  = Frequency of radiation

- ii. The idea of Quantum Physics was successfully used by Einstein to explain a completely new phenomenon called Photoelectric effect.
- iii. Neil Bohr also used the similar concept to explain the spectrum of hydrogen atom successfully.

- iv. The concept of dual nature of radiation was also extended to material particles. It was Louis de Broglie who successfully explained the nature of material particles. i.e. wave nature and particle nature.
- v. The uncertainty principle was developed by Warner Heisenberg which imposes some restrictions in the physical system. According to this principle, all the physical properties of a system cannot be determined simultaneously with a greater degree of accuracy.
- vi. According to Quantum Physics, every system is characterized by a wave function. This wave function  $\psi$  describes the system completely and satisfies a partial differential equation given by Erwin Schrodinger and is known as Schrodinger Wave Equation.
- vii. The physical state of any system was previously determined in a deterministic way using classical physics. But Max Born suggested that the state of the system can only be determined in a probabilistic way.
- viii. To incorporate the effect of special theory of relativity in quantum mechanics, Dirac formulated relativistic quantum mechanics. This leads to the development of quantum field theory which successfully describes the interaction of radiation with matter.

So, the quantum theory was successful in a wide class of physical phenomena.

## **WAVE-PARTICLE DUALITY OF MATTER**

Louis de-Broglie, a French physicist gave the suggestion that the correspondence between wave and particle is not confined to radiation only. It is also valid for material particles, like electron, proton, neutron, atoms, molecule, etc.

He stated that every moving particle is associated with the wave known as matter wave or de-Broglie wave. The principle of associating a wave with particle is called **wave-particle duality**. Mathematically,

The de-Broglie wavelength of a wave is given by,

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Where  $h$  = Planck's constant,  $p$  = momentum,  $m$  = mass of particle and  $v$  = velocity of particle

## PROOF

de-Broglie combined ideas from Quantum theory of Planck and Einstein's theory of relativity and suggested that particles have the energy associated with it is given by

$$\begin{aligned} E &= h\nu && (\text{Planck's theory; } \nu = \text{frequency of wave}) \\ \& E = mc^2 && (\text{Einstein's theory; } c = \text{velocity of light}) \end{aligned}$$

$$\begin{aligned} \text{So, } h\nu &= mc^2 \Rightarrow \frac{hc}{\lambda} = mc^2 \\ \Rightarrow \lambda &= \frac{h}{mc} = \frac{h}{p} \quad \text{---} \rightarrow (1) \quad [\because mc = p = \text{momentum}] \end{aligned}$$

For particle moving with velocity  $v$ , equation (1) can be written as

$$\lambda = \frac{h}{mv} = \frac{h}{p} \rightarrow (2)$$

## EINSTEIN'S PHOTOELECTRIC EQUATION

Einstein applied Planck's quantum theory of radiation in deriving the photoelectric equation. As per Planck, electromagnetic radiations travel in small discrete packets of energy called **Photons**. Each photon is associated with energy given by

$$E = h\nu \quad \text{---} \rightarrow (1)$$

Where,  $h$  = Planck's constant and  $\nu$  = frequency of radiation

According to Einstein when a photon falls on a photo-surface, the energy of the photon is totally absorbed by the free electrons. A part of this energy is utilized by the electrons to overcome the surface barrier forces and rest part gives kinetic energy to it is called **Work function** of the material and denoted by ' $W$ '.

If  $v$  is the velocity of the electron of mass ' $m$ ', then the kinetic energy will be  $\frac{1}{2}mv^2$ .

$$\text{So, we write } h\nu = W + \frac{1}{2}mv^2 \quad \text{---} \rightarrow (2)$$

When light of threshold frequency ' $\nu_0$ ' falls on the photo-surface, the electrons just manage to come out of the photo-metal without any kinetic energy.

For such case,  $W = h\nu_0$ .

So, equation (2) can be written as,

$$h\nu = h\nu_0 + \frac{1}{2}mv^2 \quad \text{---} \rightarrow (3)$$

$$\Rightarrow \frac{1}{2}mv^2 = h(\nu - \nu_0) \longrightarrow (4)$$

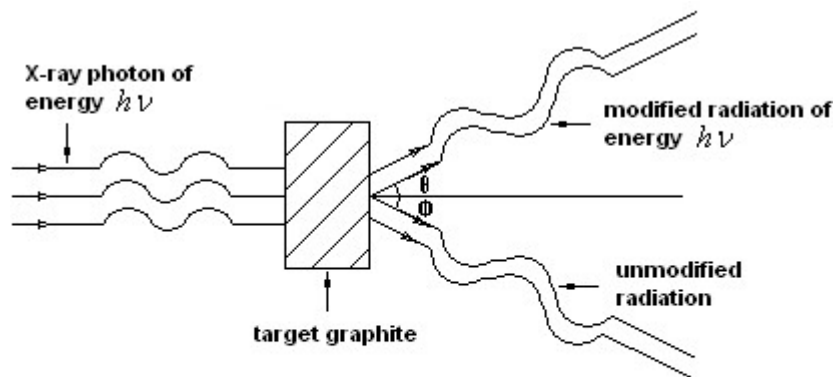
Equations (2), (3) and (4) represent **Einstein's photo-electric Equation**.

### Consequences of Einstein's equation

- From equation (34), it has been observed that more the frequency ' $\nu$ ', more is the velocity and hence kinetic energy.
- When  $\nu > \nu_0$ , the velocity becomes imaginary. i.e. no electrons can be emitted. Hence, the concept of threshold frequency was satisfactorily explained by Einstein.
- Since, the photo-electric energy is activated by the collision between photon and electrons, the phenomenon is almost instantaneous.
- If the photo-cathode is made positive and the anode is made negative, the kinetic energy of photo-electrons will be reduced, by an amount of eV (electron volt).

### COMPTON EFFECT

When a monochromatic beam of X-rays is scattered by electrons, it contains two wavelengths. One is the modified radiation (longer wavelength) and the other is the modified radiation (shorter wavelength). This splitting of X-rays due to the inelastic interaction is known as **Compton Effect**.



#### [ COMPTON EFFECT ]

$\phi$  = angle of recoil of electron

$\theta$  = scattering angle

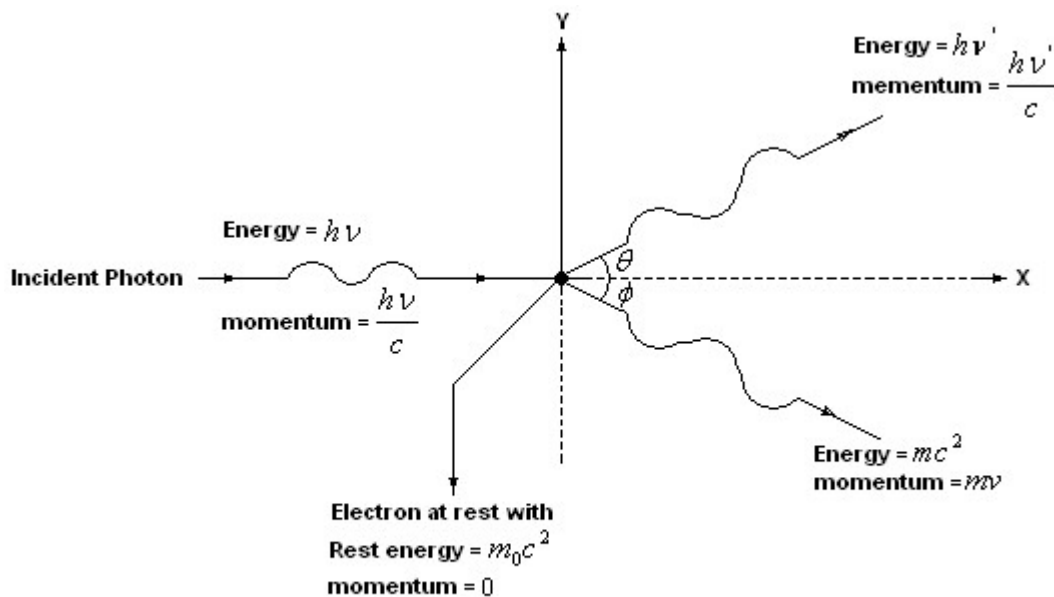
When the X-ray beams are scattered by the electrons in the graphite target, the scattered X-rays have two components.

- A component with wavelength same as that X-rays is called **unmodified or Thompson component**.
- another component called **modified or Compton component** has wavelength greater than that of the incident X-rays.

The increase of wavelength in the Compton component is called **Compton shift**( $\Delta\lambda$ ). It depends upon the angle of scattering and is independent of wavelength of the incident X-rays.

Mathematical Theory:

This effect was explained by Compton on the basis of Quantum theory of radiation by considering the entire process as a particle collision event between the incident photons and loosely bound electrons of the material. In such process, both momentum and energy are conserved.



Let,  $\theta$  = Angle of scattering,  $\lambda$  &  $\nu$  = wavelength and frequency of incident radiation

$m_0$  = rest mass of the electron,  $c$  = velocity of light

$\lambda'$  &  $\nu'$  = wavelength and frequency of the scattered radiation (modified)

$\phi$  = Angle of recoil of electrons,  $v$  = velocity of the electron.

The energy of incident photon =  $h\nu$ , Momentum of incident photon =  $\frac{h\nu}{c}$

Before collision the electron is at rest,

So, Rest energy of electron =  $m_0c^2$  and momentum = 0

After collision, the energy of scattered photon =  $h\nu'$  and momentum =  $\frac{h\nu'}{c}$

The energy of electron =  $mc^2$  and momentum =  $mv$ .

The momentum and energy in such a process is conserved. i.e. momentum and energy before collision must be equal to after collision.

The momentum has got two components. The X-component of momentum before collision must be equal to the X-component after collision.

$$\begin{aligned}\frac{h\nu}{c} + 0 &= \frac{h\nu'}{c} \cos \theta + mv \cos \phi \quad \Rightarrow mv \cos \phi = \frac{h\nu}{c} - \frac{h\nu'}{c} \cos \theta \\ \Rightarrow mvc \cos \phi &= h\nu - h\nu' \cos \theta \quad \Rightarrow mvc \cos \phi = h(\nu - \nu' \cos \theta) \\ \Rightarrow m^2 v^2 c^2 \cos^2 \phi &= h^2 (\nu - \nu' \cos \theta)^2 \rightarrow (1)\end{aligned}$$

The Y-component of momentum before and after collision is equal.

$$\begin{aligned}0 &= \frac{h\nu'}{c} \sin \theta - mv \sin \phi \\ \Rightarrow mv \sin \phi &= \frac{h\nu'}{c} \sin \theta \\ \Rightarrow m^2 v^2 c^2 \sin^2 \phi &= h^2 \nu'^2 \sin^2 \theta \rightarrow (2)\end{aligned}$$

Adding equations (1) and (2), we can get

$$\begin{aligned}m^2 v^2 c^2 \cos^2 \phi + m^2 v^2 c^2 \sin^2 \phi &= h^2 (\nu - \nu' \cos \theta)^2 + h^2 \nu'^2 \sin^2 \theta \\ \Rightarrow m^2 v^2 c^2 &= h^2 \nu^2 + h^2 \nu'^2 \cos^2 \theta - 2h^2 \nu \nu' \cos \theta + h^2 \nu'^2 \sin^2 \theta \\ \Rightarrow m^2 v^2 c^2 &= h^2 \nu^2 + h^2 \nu'^2 - 2h^2 \nu \nu' \cos \theta \\ \Rightarrow m^2 v^2 c^2 &= h^2 (\nu^2 + \nu'^2 - 2\nu \nu' \cos \theta) \rightarrow (3)\end{aligned}$$

The energies before and after collision are equal.

$$\begin{aligned}\therefore h\nu + m_0 c^2 &= h\nu' + mc^2 \quad \Rightarrow mc^2 = h(\nu - \nu') + m_0 c^2 \\ \Rightarrow m^2 c^4 &= h^2 (\nu - \nu')^2 + m_0^2 c^4 + 2h(\nu - \nu') m_0 c^2 \\ \Rightarrow m^2 c^4 &= h^2 (\nu^2 + \nu'^2 - 2\nu \nu') + m_0^2 c^4 + 2h(\nu - \nu') m_0 c^2 \rightarrow (4)\end{aligned}$$

Subtracting equation (3) from equation (4), we can write

$$\begin{aligned}m^2 c^4 - m^2 v^2 c^2 &= h^2 (\nu^2 + \nu'^2 - 2\nu \nu') - h^2 (\nu^2 + \nu'^2 - 2\nu \nu' \cos \theta) + m_0^2 c^4 + 2h(\nu - \nu') m_0 c^2 \\ \Rightarrow m^2 c^2 (c^2 - v^2) &= 2h^2 \nu \nu' \cos \theta - 2h^2 \nu \nu' + m_0^2 c^4 + 2h(\nu - \nu') m_0 c^2 \rightarrow (5)\end{aligned}$$

We know that,

$$m = \frac{m_0}{\left(1 - \frac{v^2}{c^2}\right)^{1/2}} \Rightarrow m^2 = \frac{m_0^2}{1 - \frac{v^2}{c^2}} \Rightarrow m^2 = \frac{m_0^2 c^2}{c^2 - v^2} \Rightarrow m^2 c^2 (c^2 - v^2) = m_0^2 c^4 \rightarrow (6)$$

Substituting equation (6) in equation (5), we can write

$$\begin{aligned}
 m_0^2 c^4 &= 2h^2 \nu \nu' (\cos \theta - 1) + m_0^2 c^4 + 2h(\nu - \nu') m_0 c^2 \\
 \Rightarrow 2h^2 \nu \nu' (\cos \theta - 1) &= -2h(\nu - \nu') m_0 c^2 \\
 \Rightarrow 2h(\nu - \nu') m_0 c^2 &= 2h^2 \nu \nu' (1 - \cos \theta) \\
 \Rightarrow \nu - \nu' &= \frac{h \nu \nu'}{m_0 c^2} * 2 \sin^2 \frac{\theta}{2} [\because (1 - \cos 2\theta) = 2 \sin^2 \theta] \\
 \Rightarrow \frac{\nu - \nu'}{\nu \nu'} &= \frac{2h}{m_0 c^2} * \sin^2 \frac{\theta}{2} \quad \Rightarrow \frac{1}{\nu'} - \frac{1}{\nu} = \frac{2h}{m_0 c^2} * \sin^2 \frac{\theta}{2} \\
 \Rightarrow \frac{c}{\nu'} - \frac{c}{\nu} &= \frac{2h}{m_0 c} * \sin^2 \frac{\theta}{2} \quad \Rightarrow \lambda' - \lambda = \frac{2h}{m_0 c} * \sin^2 \frac{\theta}{2} [\because c = \nu \lambda] \\
 \therefore \Delta \lambda &= 2\lambda_c \sin^2 \frac{\theta}{2} \quad \text{--- (7)}
 \end{aligned}$$

Where,  $\lambda_c$  = **Compton wavelength for electrons.**

$$\lambda_c = \frac{h}{m_0 c}$$

The increase in wavelength is called the **Compton shift**

If,  $\theta = 0 \Rightarrow \sin \theta = 0 \Rightarrow \Delta \lambda = 0$

$\Rightarrow$  There is no Compton shift along the direction of incident radiation.

If  $\theta = \pi^c \Rightarrow \sin^2 \frac{\pi}{2} = 1 \Rightarrow \Delta \lambda = 2\lambda_c$

$\Rightarrow$  Maximum value of Compton shift.

So, the Compton shift  $\Delta \lambda$  depends upon the angle of scattering which was explained by treating the incident X-ray photons as particle rather than waves. Thus, the radiation has dual character i.e. particle as well as wave.

**Problem:** Calculate the value of Compton wavelength for electron is

$$\begin{aligned}
 \lambda_c &= \frac{h}{m_0 c} \Rightarrow \lambda_c = \frac{6.626 * 10^{-34}}{9.1 * 10^{-31} * 3 * 10^8} m \\
 \Rightarrow \lambda_c &= 2.426 * 10^{-12} m = 2.426 * 10^{-2} * 10^{-10} m = 2.426 * 10^{-2} \overset{0}{A} = 0.02426 \overset{0}{A} \\
 \Rightarrow \lambda_c &= 0.02426 \overset{0}{A}
 \end{aligned}$$

## PAIR PRODUCTION

When high frequency gamma rays are allowed to pass near the atomic nuclei, some  $\gamma$  - rays are converted into electron-positron pair. This phenomenon is called **Pair production** or **Pair creation**.

The Pair production was explained by considering the  $\gamma$  -rays as photons. So, it has got energy  $h\nu$  and momentum is  $\frac{h\nu}{c}$ . After passing through the nucleus, it is converted into electron-positron pair. Positron is the ant-particle of electron which has got everything opposite to that of electron.

The rest energy of both the particles are  $2m_0c^2$ ; where  $m_0$  is the rest mass. So, the pair production to occur, the  $\gamma$  -ray photon must have energy greater or equal to  $2m_0c^2$ . The minimum energy required for formation of pair is called **Threshold frequency** denoted by ' $\nu_0$ '.

$$\text{Threshold energy} = h\nu_0 = 2m_0c^2$$

If  $\nu > \nu_0$ , then the extra energy is carried by the electron-positron pair as kinetic energy. The vector sum of the linear momentum of electron and positron is equal to the linear momentum of the  $\gamma$  -ray photon.

From Photo-electric Effect, Compton Effect and Pair production it can be concluded that the relative occurrence of the above processes depends upon the energy of radiation.

- (a). For a high frequency or high energy of radiation pair production is dominant.
- (b). for intermediate range of frequencies or energy of radiation the Compton Effect is dominant.
- (c). for low frequency radiation or lower energy, photo-electric effect is dominant.

## HEISENBERG'S UNCERTAINTY PRINCIPLE

In classical physics, the position and momentum of particles can be measured with greater degree of accuracy. But in case of quantum mechanics when a particle moves, then a wave associated with the particles also moves. Since, the wave is a spread out distribution; so the position and momentum of the particle cannot be measurement simultaneously with greater degree of accuracy. There lies an uncertainty in the measurement of position and momentum. This uncertainty was explained by Heisenberg and the principle is called **Heisenberg's uncertainty principle**.

It states that the position and momentum of a particle cannot be measurement simultaneously with higher degree of accuracy.

If  $\Delta x$  = uncertainty in the measurement of position of the particle along X-axis

&  $\Delta P_x$  = uncertainty in the measurement of the X-component of the linear momentum, then the uncertainty relation is given by



$$\Delta x. \Delta P_x \geq \frac{\hbar}{2} \rightarrow (1) \quad [ \because \hbar = \frac{h}{2\pi} ]$$

Similarly, for Y and Z components,

$$\Delta y. \Delta P_y \geq \frac{\hbar}{2} \rightarrow (2)$$

$$\& \quad \Delta z. \Delta P_z \geq \frac{\hbar}{2} \rightarrow (3)$$

In general, 
$$\Delta r. \Delta P_r \geq \frac{\hbar}{2} \rightarrow (4)$$

Where,  $r$  is for X, Y and Z components

Here  $\Delta x$  and  $\Delta P_x$  are two complementary observables i.e. an exact measurement in the value of one observable can be obtained by the uncertainty in the measurement of another observable.

$$\Delta t. \Delta E \geq \frac{\hbar}{2} \rightarrow (5)$$

Equation (4) represents the position-momentum uncertainty relation. Equation (5) represents the time-energy uncertainty relation.

## APPLICATION OF UNCERTAINTY PRINCIPLE

### 1. GROUND STATE ENERGY OF HARMONIC OSCILLATION

The energy of one-dimensional linear harmonic oscillator is

$$\begin{aligned} E &= E_k + E_p \\ \Rightarrow E &= \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x^2 \rightarrow (1) \end{aligned}$$

Where  $m$  is the mass,  $\omega$  is the angular frequency,  $P$  is the momentum and  $x$  is the displacement of the particle.

According to uncertainty principle

$$\Delta x. \Delta P_x \approx \frac{\hbar}{2} \quad \Rightarrow \quad x. P \approx \frac{\hbar}{2} \quad \Rightarrow \quad P \approx \frac{\hbar}{2x}$$

$$\therefore E = \frac{P^2}{2m} + \frac{1}{2}m\omega^2 x^2 \quad \Rightarrow \quad E = \frac{\hbar^2}{8mx^2} + \frac{1}{2}m\omega^2 x^2 \quad \text{--- -- -- --} \rightarrow (2)$$

In ground state, the energy is minimum.

Let,  $x_0$  be the displacement of the particle in the ground state.

$$\therefore \left( \frac{\partial E}{\partial x} \right)_{x=x_0} = 0$$

[ For a function having maxima or minima at a point, the first order derivative at that point is zero]

Now,

$$\frac{\partial E}{\partial x} = \frac{\partial}{\partial x} \left[ \frac{\hbar^2}{8mx^2} + \frac{1}{2}m\omega^2x^2 \right] \Rightarrow \frac{\partial E}{\partial x} = -\frac{\hbar^2}{4mx^3} + m\omega^2x$$

$$\begin{aligned} \text{At } x = x_0, \quad \left( \frac{\partial E}{\partial x} \right) = 0 &\Rightarrow \left( \frac{\partial E}{\partial x} \right)_{x=x_0} = -\frac{\hbar^2}{4mx_0^3} + m\omega^2x_0 = 0 \\ &\Rightarrow -\frac{\hbar^2}{4mx_0^3} + m\omega^2x_0 = 0 \quad \Rightarrow \frac{\hbar^2}{4mx_0^3} = m\omega^2x_0 \\ &\Rightarrow \frac{\hbar^2}{4m^2\omega^2} = x_0^4 \quad \Rightarrow x_0^2 = \frac{\hbar}{2m\omega} \quad \text{--- --} \rightarrow (3) \end{aligned}$$

Substituting the value of  $x_0^2$  in equation (2), the ground state energy of harmonic oscillator can be obtained as

$$\begin{aligned} E &= \frac{\hbar^2}{8mx_0^2} + \frac{1}{2}m\omega^2x_0^2 \quad \Rightarrow E = \frac{\hbar^2}{8m \frac{\hbar}{2m\omega}} + \frac{1}{2}m\omega^2 \frac{\hbar}{2m\omega} \\ &\Rightarrow E = \frac{\hbar\omega}{4} + \frac{\hbar\omega}{4} \quad \Rightarrow E = \frac{\hbar\omega}{2} \Rightarrow E = \frac{1}{2} \frac{\hbar}{2\pi} \times 2\pi\nu \quad \Rightarrow E = \frac{1}{2} \hbar\nu \rightarrow (4) \end{aligned}$$

This is the energy of harmonic oscillator in the ground state which means that the particle is always in motion which was not explained in classical physics.

## 2. ELECTRON IS NOT A NUCLEAR CONSTITUENT

Kinetic energy of the electron of mass 'm' is

$$\begin{aligned} E_K &= \frac{p^2}{2m} \quad \Rightarrow E_K = \frac{\hbar^2}{8mx^2} [\because x.P \approx \frac{\hbar}{2} \text{ From uncertainty principle}] \\ &\Rightarrow E_K = \frac{(6.626 \times 10^{-34})^2}{8 \times 9.11 \times 10^{-31} \times 4 \times (3.14)^2 \times (10^{-14})^2} \text{ MeV} = 20 \text{ MeV}. \end{aligned}$$

[ $\because$  'x' is the radius of nucleus here and the uncertainty in the position of the electron inside the nucleus is the radius of the nucleus is  $10^{-14}$  m.]

So, the electron to be a nuclear constituent, its energy must be greater or equals to  $20\text{MeV}$ . But experimental data represents that the electron in an atom should not have energy greater than  $4\text{MeV}$ . Therefore, electron is not a nuclear constituent.

## TRANSITION FROM DETERMINISTIC STATE TO PROBABILISTIC STATE

In classical physics, the physical properties of a system can be specified exactly at least in principle. If the initial conditions of a system are known, its subsequent configuration can be determined by using the laws of physics applicable to the system. Thus, classical physics is deterministic in nature.

But, according to Quantum theory, the wave nature of particle associates the wave packet with each particle. Therefore, the particle becomes an entity spread out in space leading to uncertainty in the position. If the position is exactly determined then the momentum and hence the velocity becomes infinitely uncertain. So, the uncertainty principle imposes restriction on the exact values of the physical quantities. So, in Quantum mechanics, the physical quantities are described in a probabilistic manner. i.e. there always lies the probability of determining the physical parameters associated with the particle. Here the observed value is the average of different values. For example, if a system has allowed energy  $E_1, E_2, E_3 \& E_4$  with probabilities 0.25, 0.1, 0.5 and 1.5, then the observed energy

$$\langle E \rangle = 0.25E_1 + 0.1E_2 + 0.5E_3 + 1.5E_4$$

As the state of a system changes with time, the relative probabilities corresponding to different energies changes. Hence observed energy also changes. Thus, behavior of physical system is determined by the relative probabilities associated with the allowed values of physical quantities. This probabilistic description is the basic characteristics of quantum physics and is achieved by the wave function.

## WAVE FUNCTION AND ITS PHYSICAL SIGNIFICANCE

As per de-Broglie, every matter is associated with a matter that consists of standing waves in its neighborhood. So, a mathematical reformation using a wave function is required. Such a mathematical reformation is known as wave mechanics or quantum mechanics. It was developed by *Erwin Schrodinger* in 1926. He described the amplitude of matter waves by a complex quantity

‘ $\psi$ ’ known as Schrodinger function or wave function or state of a system. It is a function of position and time and it describes the particular dynamical system under observation.

$$\psi = \psi(\vec{r}, t)$$

For quantum mechanical description, every physical system is characterized by a wave function  $\psi(\vec{r}, t)$ , which contains all the information about the system.

## PROPERTIES OF WAVE FUNCTION

1. Wave functions are the mathematical representation of particles which contains all the information required for the probabilistic description of the particles.
2. ‘ $\psi$ ’ must be well observed. i.e.,
  - a. It must be single valued at each and every point.
  - b. It should not have the value infinity at any point.
  - c. It should be continuous at each and every point along with its derivative.
3. Its absolute value at any point should be such that

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(x, y, z) \psi^*(x, y, z) dx dy dz = \int_v \psi \psi^* dv = 1$$

[Where  $\psi^*$  is the complex conjugate of  $\psi$ ]

- a. This represents normalization condition that is there lies the probability of finding the particle in the state  $\psi$ .
- b. If  $\int_v \psi \psi^* dv = 0$  then the particle cannot be found in space. (means in the state  $\psi$ )

This is called orthogonal condition.

Combining the above two equations we can write

$$\int_v \psi_m \psi_n^* dv = \delta_{mn} = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

This is called **Ortho-normal condition**.

4. It can take real or imaginary value.
5. Any operator when operates on a wave function the result gives rise to a value along with the wave function. This is called **Eigen value** of the operator for the function ‘ $\psi$ ’ and the wave function is known as **Eigen function**.

Example:  $\hat{A}\psi = a\psi$

Where,  $\hat{A}$  is the operator,

$\psi$  is the wave function,

$a$  is the Eigen value of the operator.

6.  $|\psi|^2$  gives the probability of finding the particle and therefore it is essential to calculate the expectation value of the dynamical quantity. The expectation value of an observable corresponding to the operator  $\hat{A}$  of a physical system in the state  $\psi$  is

$$\langle A \rangle = \frac{\int \psi^* \hat{A} \psi dv}{\int \psi \psi^* dv}$$

## PROBABILITY DENSITY

The probability of finding the particle per unit volume of a system being in the state ' $\psi$ ' is called probability density.

Mathematically, probability density =  $|\psi|^2$

So, probability of finding the particle in the volume ' $dv$ ' =  $|\psi|^2 \cdot dv$

And hence the probability of finding the particle in the entire volume ' $v$ ' =  $\int_v |\psi|^2 dv$

According to normalization condition, the particle is to be found somewhere in space.

Therefore,  $\int_v |\psi|^2 dv = 1$ .

The unit of  $|\psi|^2$  in 3-D is  $cm^{-3}$  and dimension =  $[M^0 L^{-3} T^0]$  So,  $\psi$  has the dimension  $[M^0 L^{-3/2} T^0]$

In 2-D,  $|\psi|^2$  has dimension  $[M^0 L^{-2} T^0]$  and  $\psi$  has the dimension  $[M^0 L^{-1} T^0]$ .

In 1-D,  $|\psi|^2$  has dimension  $[M^0 L^{-1} T^0]$  and  $\psi$  has the dimension  $[M^0 L^{-1/2} T^0]$ .

## EIGEN VALUE

The set of allowed values of a physical quantity for a given system is called the **Eigen values** of the quantity for the system. (Eigen means proper).

For example, in hydrogen atom, the electron can have some specific allowed values of energy. These are called **Energy Eigen values**. The Eigen values are always real quantities and they can take up discrete and continuous values.

## EIGEN FUNCTION

The allowed quanta states of physical systems are called the **Eigen states** and are represented by a set of functions are called **Eigen functions**.

The actual wave function of a system in a given state is a linear combination of the Eigen functions associated with each state. Eigen functions of a system obey the corresponding Schrodinger equation and are obtained as the solution of the equation with proper boundary conditions.

## OPERATORS

Every physical quantity is associated with a quantum mechanical operator. These operators operate on the Eigen function to give corresponding Eigen values which are nothing but the physical quantities or observables.

Operators corresponding to the different physical quantities are given below:

PHYSICAL QUANTITY	OPERATOR
1. Position vector ( $\vec{r}$ )	1. Position operator ( $\hat{r}$ )
2. Linear momentum ( $\vec{P}$ )	2. Linear momentum operator ( $\hat{P}$ ): In 3-D, $\hat{P} = -i\hbar \vec{\nabla}$ In 1-D, $\hat{P}_x = -i\hbar \frac{\partial}{\partial x}$ , $\hat{P}_y = -i\hbar \frac{\partial}{\partial y}$ and $\hat{P}_z = -i\hbar \frac{\partial}{\partial z}$
3. Kinetic energy ( $T$ )	3. Kinetic energy operator ( $\hat{T}$ ): In 3-D, $\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$ In 1-D, $\hat{T}_x = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$ , $\hat{T}_y = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2}$ and $\hat{T}_z = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2}$
4. Potential energy ( $V$ )	4. Potential energy operator ( $\hat{V}$ )
5. Total energy ( $E$ )	5. Total energy operator ( $\hat{E}$ ): $\hat{E} = \hat{T} + \hat{V} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \right]$ or, $\hat{E} = i\hbar \frac{\partial}{\partial t}$
6. Angular momentum ( $\vec{L}$ )	6. Angular momentum operator ( $\hat{L}$ ):

	$\hat{L}_y = -i\hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right)$ $\hat{L}_z = -i\hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$
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## EXPECTATION VALUE

It is defined as the mathematical expectation for the result of the single measurement or it is the average of the large number of measurements on the independent systems.

Let  $f(x)$  be any function, then its expectation value is given by,

$$\langle f(x) \rangle = \frac{\int \psi^* f(x) \psi dv}{\int \psi \psi^* dv}$$

If  $\psi$  is normalized then,

$$\int \psi \psi^* dv = 1$$

And hence,

$$\langle f(x) \rangle = \int \psi^* f(x) \psi dv$$

## EXPECTATION VALUES OF DIFFERENT PHYSICAL QUANTITIES

### 1. Position:

$$\text{In 3-D, } \langle r \rangle = \int \psi^* r \psi dv$$

$$\text{In 1-D, } \langle x \rangle = \int \psi^* x \psi dv \quad \langle y \rangle = \int \psi^* y \psi dv \quad \langle z \rangle = \int \psi^* z \psi dv$$

### 2. Momentum:

$$\text{In 3-D, } \langle P \rangle = \int \psi^* \hat{P} \psi dv = \int \psi^* (-i\hbar \vec{\nabla}) \psi dv = -i\hbar \int \psi^* \vec{\nabla} \psi dv$$

$$\text{In 1-D, } \langle P_x \rangle = \int \psi^* \left( -i\hbar \frac{\partial}{\partial x} \right) \psi dv = \int \psi^* \left( -i\hbar \frac{\partial}{\partial y} \right) \psi dv = \int \psi^* \left( -i\hbar \frac{\partial}{\partial z} \right) \psi dv$$

### 3. Energy:

$$\text{In 3-D} \quad \langle E \rangle = \int \psi^* \hat{E} \psi dv = \int \psi^* \left[ -\frac{\hbar^2}{2m} \nabla^2 + \hat{V} \right] \psi dv$$

$$\text{In 1-D, } \langle E_x \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} + \hat{V} \right) \psi dv \quad \langle E_y \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \hat{V} \right) \psi dv$$

$$\text{and} \quad \langle E_z \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \hat{V} \right) \psi dv$$

### 4. Kinetic energy :

$$\text{In 3-D,} \quad \langle T \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \psi dv$$

$$\text{In 1-D,} \quad \langle E_x \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \right) \psi dv \quad \langle E_y \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial y^2} \right) \psi dv$$

$$\text{and} \quad \langle E_z \rangle = \int \psi^* \left( -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \right) \psi dv$$

**Question:** The probabilities that a system can be in the states represented by the Eigen function  $\psi_1, \psi_2$  &  $\psi_3$  are  $\frac{1}{2}, \frac{1}{3}$  &  $\frac{1}{6}$  respectively. Write down the wave function for the system and find out the expectation values of energy for the energies  $4eV, 6eV$  and  $9eV$ .

**Solution:** The probability of finding the particle in state  $\psi_1$  is  $\frac{1}{2}$ .

Similarly, the probability of finding the particle in state  $\psi_2$  and  $\psi_3$  is  $\frac{1}{3}$  and  $\frac{1}{6}$  respectively.

So, here

$$C_1^2 = \frac{1}{2}, C_2^2 = \frac{1}{3}, C_3^2 = \frac{1}{6}$$

$$\Rightarrow C_1 = \frac{1}{\sqrt{2}}, C_2 = \frac{1}{\sqrt{3}}, C_3 = \frac{1}{\sqrt{6}}$$

$$\text{Now,} \quad \psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3$$

$$\Rightarrow \psi = \frac{1}{\sqrt{2}}\psi_1 + \frac{1}{\sqrt{3}}\psi_2 + \frac{1}{\sqrt{6}}\psi_3$$

The expectation value of the energy is given by,

$$\langle E \rangle = C_1^2 E_1 + C_2^2 E_2 + C_3^2 E_3 = \left( \frac{1}{2} \times 4 + \frac{1}{3} \times 6 + \frac{1}{6} \times 9 \right) eV$$

$$= \left( 2 + 2 + \frac{3}{2} \right) eV = \left( 4 + \frac{3}{2} \right) eV = \frac{11}{2} eV$$

$$\Rightarrow \langle E \rangle = 5.5 eV$$

## SCHROEDINGER'S WAVE EQUATION

It is a differential equation which is capable of describing the motion of particles. It was developed by Schroenger.

There are two types of Schrodinger equation.

1. Time independent Schrodinger wave equation



## 2. Time dependent Schrodinger wave equation

### TIME INDEPENDENT SCHODINGER WAVE EQUATION

Let  $\psi$  be the wave function that describes the wave associated with the particle. From Bohr's correspondence principle we know that  $\psi$  also satisfies the classical wave equation given by

$$\nabla^2 \psi = \frac{1}{V^2} \frac{\partial^2 \psi}{\partial t^2} \quad \text{--- -- -- -- --} \rightarrow (1)$$

The wave function  $\psi$  can be also written as  $\psi = \psi_0 e^{-i\omega t}$

Now,  $\frac{\partial \psi}{\partial t} = -i\omega \psi_0 e^{-i\omega t} = (-i\omega)(-i\omega) \psi_0 e^{-i\omega t} = -\omega^2 \psi \quad \text{--- -- -- --} \rightarrow (2)$

Substituting equation (2) in equation (1),

$$\nabla^2 \psi = \frac{1}{V^2} \frac{\partial^2 \psi}{\partial t^2} = -\frac{\omega^2}{V^2} \psi \quad \Rightarrow \nabla^2 \psi = -\frac{4\pi^2 \nu^2}{\lambda^2} \psi \quad [\because \omega = 2\pi\nu \text{ \& } V = \lambda\nu]$$

$$\Rightarrow \nabla^2 \psi = -\frac{4\pi^2}{\lambda^2} \psi = -\frac{4\pi^2}{h^2 / m^2 \nu^2} \psi \quad [\because \lambda = \frac{h}{P} = \frac{h}{m\nu}]$$

$$\Rightarrow \nabla^2 \psi = \frac{-2 \times \frac{1}{2} m \nu^2 \times m \psi}{\hbar^2} \quad \text{--- -- -- --} (3) \quad [\because \hbar = \frac{h}{2\pi}]$$

We know that, total energy

$$E = K.E + P.E = T + V = \frac{1}{2} m \nu^2 + V \quad \Rightarrow \frac{1}{2} m \nu^2 = (E - V)$$

Putting this value in equation (3), we get

$$\begin{aligned} \therefore \nabla^2 \psi &= -\frac{2m}{\hbar^2} \cdot \frac{1}{2} m \nu^2 \cdot \psi = -\frac{2m}{\hbar^2} (E - V) \psi \\ \Rightarrow \nabla^2 \psi + \frac{2m}{\hbar^2} (E - V) \psi &= 0 \rightarrow (3) \end{aligned}$$

This represents Schrodinger's time independent equation.

This equation can be applied for determining the total energy of a particle when it is moving in a field so that its potential is defined in terms of space coordinates.

Like other differential equations it is also governed by boundary conditions.

## TIME DEPENDENT SCHROEDINGER'S WAVE EQUATION

Let us consider a wave function given by,  $\psi = \psi_0 e^{-i\omega t}$

$$\text{Now, } \frac{\partial \psi}{\partial t} = (-i\omega)\psi_0 e^{-i\omega t} \Rightarrow \frac{\partial \psi}{\partial t} = -2\pi\nu i\psi_0 e^{-i\omega t} \quad [\because \omega = 2\pi\nu]$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} 2\pi\hbar\nu\psi_0 e^{-i\omega t} \Rightarrow \frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} h\nu\psi_0 e^{-i\omega t} \quad [\because \hbar = \frac{h}{2\pi}]$$

$$\Rightarrow i\hbar \frac{\partial \psi}{\partial t} = h\nu\psi_0 e^{-i\omega t} \Rightarrow i\hbar \frac{\partial \psi}{\partial t} = E\psi \rightarrow (1) \quad [\because E = h\nu]$$

Now the time independent Schrodinger's equation is

$$\nabla^2 \psi + \frac{2m}{\hbar^2} (E - V)\psi = 0 \Rightarrow \frac{\hbar^2}{2m} \nabla^2 \psi + E\psi - V\psi = 0$$

$$\Rightarrow \frac{\hbar^2}{2m} \nabla^2 \psi - V\psi = -E\psi \Rightarrow \left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = E\psi$$

[09

$$\Rightarrow \left[ -\frac{\hbar^2}{2m} \nabla^2 + V \right] \psi = i\hbar \frac{\partial \psi}{\partial t} \quad \text{---} \rightarrow (2) \quad [\text{Using equation (1)}]$$

Equation (2) represents time dependent Schrodinger's wave equation.

## APPLICATION OF QUANTUM MECHANICS

### 1. FREE PARTICLE OR PARTICLE MOVING IN FORCE FREE SPACE:

Free particle is a particle which is not affected by an external field or external force. So, its potential is constant and for convenience it is taken as zero.

That is,  $V = 0$

The time independent Schrodinger's equation for a free particle can be written as

$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2} (E - V) \psi &= 0 \quad \Rightarrow \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2} \psi = 0 \\ \Rightarrow \quad \frac{\partial^2 \psi}{\partial x^2} + k^2 \psi &= 0 \quad \text{--- -- -- --} \rightarrow (1)\end{aligned}$$

$$\text{Where, } k^2 = \frac{2mE}{\hbar^2} \quad \Rightarrow \quad k = \frac{\sqrt{2mE}}{\hbar} = \text{Propagation constant}$$

Equation (1) is the second order partial differential equation whose solution can be written as

$$\psi = A_1 e^{ikx} + A_2 e^{-ikx} \quad \text{--- -- -- --} \rightarrow (2)$$

Where  $A_1, A_2$  are constants whose values can be obtained by using boundary conditions. The first part in the equation represents a plane wave propagating along positive X-direction and second part represents plane wave propagating along negative X-direction.

$$\text{Now, } k^2 = \frac{2mE}{\hbar^2} \Rightarrow 2mE = k^2 \hbar^2 \Rightarrow E = \frac{k^2 \hbar^2}{2m} \quad \text{--- -- --} \rightarrow (3)$$

The momentum is,  $\vec{P} = \hbar \vec{k}$

Since the propagation constant or propagation vector is arbitrary and can take up any value, so the energy of a free particle can take up any value and hence it is continuous.

## 2. A FREE PARTICLE MOVING IN A BOX

### (POTENTIAL WELL OF INFINITE HEIGHT AND WIDTH 'L')

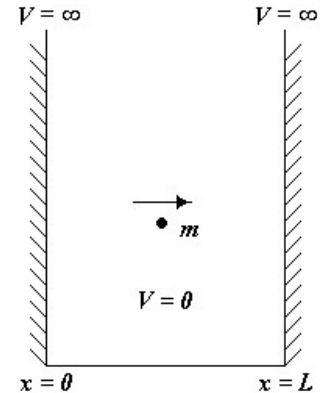
Consider a free particle of mass ' $m$ ' moving freely inside a potential well of infinite height and width ' $L$ '.

Since the particle is free inside the well, so the potential is constant and it is taken as zero for convenience. But outside the well the potential is infinite.

The potential is taken as

$$V(x) = \begin{cases} 0 & \text{for } 0 < x < L \\ \infty & \text{otherwise} \end{cases}$$

Let  $E$  be the energy of the particle. Now, the one-dimensional time independent Schrodinger's equation such a system can be written as,



$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} + \frac{2m}{\hbar^2}(E - V)\psi &= 0 \quad \Rightarrow \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{2mE}{\hbar^2}\psi = 0 \quad [\because V = 0] \\ \Rightarrow \frac{\partial^2 \psi}{\partial x^2} + k^2\psi &= 0 \quad \text{--- -- -- --} \rightarrow (1)\end{aligned}$$

Equation (1) is the second order partial differential equation whose solution can be written as

$$\psi(x) = A \cos kx + B \sin kx \quad \text{--- -- -- --} \rightarrow (2)$$

Where  $A$  and  $B$  are constants whose values can be obtained by using boundary conditions.

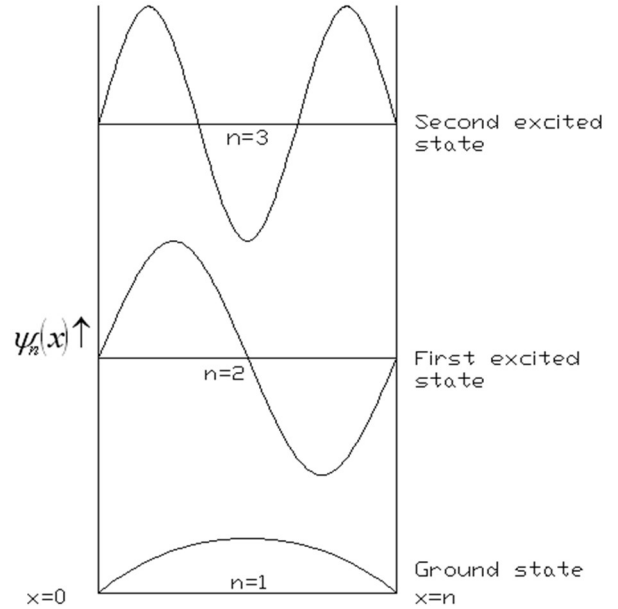
The boundary conditions are  $\psi(x)|_{x=0} = 0$  and  $\psi(x)|_{x=L} = 0$

$$\text{At } x=0, \quad \psi(x) = 0 \Rightarrow A \cos 0 + B \sin 0 = 0 \Rightarrow A = 0$$

$$\begin{aligned}\text{At } x=L, \quad \psi(x) = 0 &\Rightarrow A \cos kL + B \sin kL = 0 \Rightarrow B \sin kL = 0 \\ &\Rightarrow \sin kL = 0 \quad [\because B \neq 0 \text{ for wave function to exist}] \\ &\Rightarrow kL = n\pi \quad \Rightarrow k = \frac{n\pi}{L} \quad \text{--- -- -- --} \rightarrow (3) \quad \text{Where, } n = 1, 2, 3, \dots\end{aligned}$$

The value of  $B$  can be obtained by using normalization condition.

$$\begin{aligned}\int_0^L |\psi(x)|^2 dx &= 1 \\ \Rightarrow \int_0^L B^2 \sin^2 kx dx &= 1 \\ \Rightarrow B^2 \int_0^L \sin^2 kx dx &= 1 \\ \Rightarrow B^2 \int_0^L \left( \frac{1 - \cos 2kx}{2} \right) dx &= 1 \\ \Rightarrow B^2 \left[ \frac{x}{2} - \frac{\sin 2kx}{2k} \right]_0^L &= 1 \\ \Rightarrow B^2 \left[ \frac{L}{2} \right] &= 1 \quad \Rightarrow B = \sqrt{\frac{2}{L}}\end{aligned}$$



So, total wave function or the general solution for the wave function is

$$\psi(x) = A \cos kx + B \sin kx \quad \Rightarrow \psi_n(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi}{L} x \rightarrow (4)$$

$$\text{For } n = 1, \quad x = \frac{L}{2}, \quad \psi(x) = \sqrt{\frac{2}{L}}$$

$$\text{For } n = 2, \quad x = \frac{L}{4}, \quad \psi(x) = \sqrt{\frac{2}{L}} \quad \text{and so on.}$$

The diagram showing nature of wave function for a free particle in potential b for different quantum state. For  $n = 1$ , the state is called **ground state**. For other values of 'n' it represents different excited states.

Now the probability density for different values of 'n' can be obtained as follows.

$$\text{Probability density} = |\psi_n(x)|^2 = \left[ \sqrt{\frac{2}{L}} \left\{ \sin\left(\frac{n\pi}{L}\right)x \right\} \right]^2 = \frac{2}{L} \left\{ \sin\left(\frac{n\pi}{L}\right)x \right\}^2 \longrightarrow (5)$$

The probability of finding the particle inside the well for different values of  $n$  is represented by the diagram given below.

From equation (3),

$$k = \frac{n\pi}{L}$$

$$\Rightarrow \frac{\sqrt{2mE}}{\hbar} = \frac{n\pi}{L}$$

$$\Rightarrow \sqrt{2mE} = \frac{n\pi\hbar}{L}$$

$$\Rightarrow 2mE = \frac{n^2\pi^2\hbar^2}{L^2}$$

$$\Rightarrow E = \frac{n^2\pi^2\hbar^2}{2mL^2} \rightarrow (6)$$

$$\Rightarrow E = \frac{\pi^2 \times \frac{\hbar^2}{4\pi^2} \times n^2}{2mL^2} \left[ \because \hbar = \frac{h}{2\pi} \right]$$

$$\Rightarrow E_n = \frac{h^2}{8mL^2} (n^2) \longrightarrow (7)$$

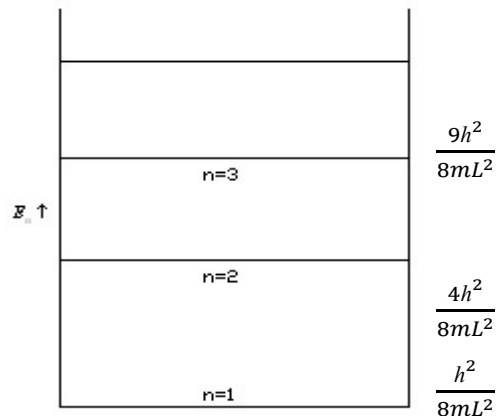
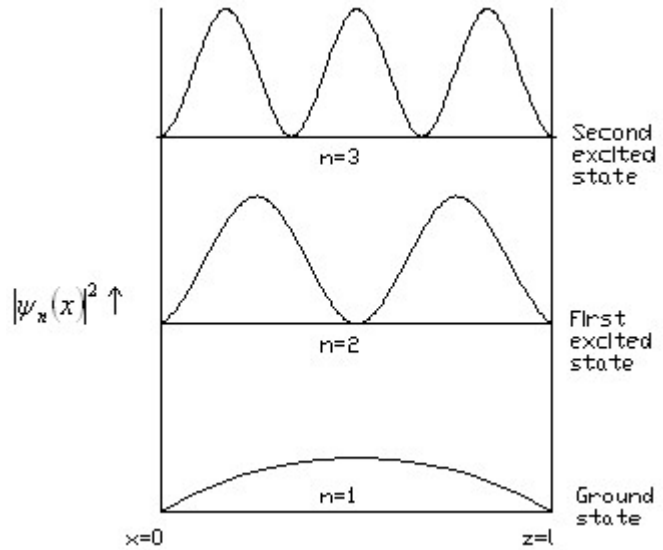
$$\text{For } n = 1, E_1 = \frac{h^2}{8mL^2}$$

$$n = 2, E_2 = \frac{4h^2}{8mL^2}$$

$$n = 3, E_3 = \frac{9h^2}{8mL^2} \text{ and so on}$$

### CONCLUSION:

1. The particle in one-dimensional potential well cannot possess any arbitrary amount of energy. That is the energy values are obtained in discrete sets only. So, the energy is quantized.



2. Also the minimum energy of particle  $E_1 = \frac{h^2}{8mL^2}$  implies that the particle in the ground state also possesses some amount of energy which was not explained classically.
3. From probability density curve, it is clear that  $|\psi(x)|^2 = 0$  at  $x = 0$  and  $x = L$  which implies that there lies probability in finding the position of the particle.